

1 **An ORGANIC LOW K DIELECTRIC ETCH WITH NH₃ CHEMISTRY**2 **Background of Invention**3 **1) Field of the Invention**

4 This invention relates generally to fabrication of
5 semiconductor devices and more particularly to the etching of
6 organic low -k dielectric layers and particularly an etch
7 process for organic low K layers that uses a ammonia based
8 chemistry (e.g., pure ammonia or ammonia with (H₂ or N₂)).

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10 **2) Description of the Prior Art**

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12 Traditional etch chemistry for the organic low-k
13 material is N₂ related chemistry, such a s N₂/O₂ and H₂ /H₂ etc.
14 The excellent physical profile of the damascene structure can be
15 obtained by N₂/H₂ chemistry with a lower etch rate, compared to
16 N₂/O₂ chemistry. However, it is very likely to get a bowing
17 sidewall profiles (e.g., non-vertical sidewalls) by N₂ /O₂
18 chemistry.

19 The importance of overcoming the various
20 deficiencies noted above is evidenced by the extensive
21 technological development directed to the subject, as documented
22 by the relevant patent and technical literature. The closest
23 and apparently more relevant technical developments in the
24 patent literature can be gleaned by considering US
25 6,071,815(Kleinhenz et al.) that shows a silicon oxide layer
26 etch that uses HF and ammonia in combination with other gases.

27 US 5,897,377(Suzuki) shows a surface treatment etch.

28 US 5,972,235(Brigham et al.) shows a low-k etch.

1 US 6,063,712(Gilton et al.) teaches an oxide etch
2 using ammonia a fluorine containing compound and a boron
3 containing compound.

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6 However, further improvement is needed to etch
7 organic low-K materials.

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2 **Summary of the Invention**3 It is an object of the present invention to provide
4 a method for etching low -k dielectric layers.5 It is an object of the present invention to provide
6 a method for etching low -k dielectric layers that uses an
7 ammonia based chemistry.8 It is an object of the present invention to provide
9 a method for etching low -k dielectric layers that uses an pure
10 ammonia or NH₃ /H₂ or NH₃ /N₂ etch gasses plus optionally CO
11 and/or O₂ .12 To accomplish the above objectives, the present
13 invention provides a method which is characterized as follows.
14 An organic low k dielectric layer is formed over a substrate. A
15 resist pattern is formed over the low k dielectric layer. The
16 resist pattern has an opening.17 Using the invention's etch process, the organic low
18 k dielectric layer is etched through the opening in an etch
19 mask. The invention's etch process comprise a NH₃ containing
20 plasma etch (optionally with H₂ or N₂).21 The invention's NH₃ containing plasma etch etches
22 Low- k materials unexpectedly well. The invention's NH₃ only
23 etch had a 30 to 80% higher etch rate than conventional N₂/H₂
24 etches of low-k materials like Silk™.25 Additional objects and advantages of the invention
26 will be set forth in the description that follows, and in part
27 will be obvious from the description, or may be learned by
28 practice of the invention. The objects and advantages of the
29 invention may be realized and obtained by means of

1 instrumentalities and combinations particularly pointed out in
2 the append claims.

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2 **Brief Description of the Drawings**

3 The features and advantages of a semiconductor
4 device according to the present invention and further details of
5 a process of fabricating such a semiconductor device in
6 accordance with the present invention will be more clearly
7 understood from the following description taken in conjunction
8 with the accompanying drawings in which like reference numerals
9 designate similar or corresponding elements, regions and
10 portions and in which:

11 Figures 1 and 2 are cross sectional views for
12 illustrating an etch process for etching organic low k materials
13 in a single damascene structure according to the present
14 invention.

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16 Figures 3 and 5 are cross sectional views for
17 illustrating an etch process for etching organic low k materials
18 in a dual damascene structure according to the present
19 invention.

20 FIG 6A shows the chemical structure for PAE.

21 FIG 6B shows the chemical structure for SilkTM (A
22 PAE containing organic dielectric with aromatic rings).

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2 **Detailed Description of the Preferred Embodiments**3 **I. Overview - NH₃ based etch for organic low K dielectric
4 layers**

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6 To accomplish the above objectives, the present
7 invention provides a method for etching organic low-k dielectric
8 layers which is characterized as follows.

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10 **organic low K compositions**

11 The invention is an ammonia etch (NH₃) chemistry
12 for organic low K layers. "Low K" means dielectric constants
13 less than or equal to 3.0. The organic low k dielectric layers
14 can be any organic dielectric material with a dielectric
15 constant less than or equal to 3.0 . These dielectric layers
16 are made from organic containing reactants. Examples of two
17 types of low k materials are: 1) organic /Spin on (e.g., K = ~
18 2.6 to 2.7 (SilkTM and FlareTM by made by Allied signal (e.g.,
19 fluorinated arylether)) and 2) oxide/CVD (k= 2.7 to 3.0) (e.g.,
20 Black diamondTM, coralTM etc. e.g., carbon doped oxides)

21 Other organic low k materials are PAE II,
22 Benzocyclobuthene (BCB), amorphous teflon
23 (Polytetrafluoroethylene) and Parylene. Also, HOSPTM from
24 AlliedSignal , hydrogen silsequioxane (HSQ) for example FOxtm
25 flowable oxide brand HSQ.

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1 One such organic low k dielectric layer is comprised
2 of poly arylene ether (PAE) possibly with other functional
3 groups - See FIG 6A for the chemical structure of PAE.

4 FIG 6B shows the chemical structure of SILKTM
5 (e.g., SilkTM made by Dow chemical). Another example of a low-
6 k dielectric. SilkTM has aromatic groups which can be etched with
7 O₂ based H₂ /H₂ and NH₃ based chemistries. It is possible that
8 N_xH_y and H radicals attack the rings during the etch.

9 The invention's NH₃ containing etch is preferably
10 used to PAE containing low K materials such as SilKtm and Flaretm.

A. Etch process - 1st embodiment - NH₃ only

11 In a first embodiment of the invention's NH₃
12 containing etch, the etch process comprises: etching the low k
13 dielectric layer 20 by applying a plasma power and flowing only
14 NH₃ gas. It is critical that only NH₃ gas is flowed. It is not
15 proper to use another N and/or H containing gas such as N₂/H₂.

16 The 1st embodiment uses NH₃ only with a power in
17 between 500 and 1500 W, medium plasma power plasma density
18 between 1E9 and 1E11 cm⁻³ and a NH₃ flow between 50 and 300 sccm
19 and a pressure between 80 and 800 mTorr. Typical process is
20 power 1000 W and a NH₃ flow 200 sccm and a pressure 100 mTorr
21 (all values range +/- 5).

22 Also the 1st embodiment forms a substantially
23 vertical sidewall (between 87 and 93 degrees to the surface of
24 the substrate.

1 **B. second embodiment NH₃ and H₂**

2 In a second embodiment, etch process comprises:
3 etching the low k dielectric layer (e.g. 20, FIG 1) by applying
4 a medium plasma density between 1E9 and 1E11 cm⁻³ and flowing NH₃
5 gas and H₂ gas.

6 The 2ND embodiment uses NH₃ and H₂ with a plasma
7 power between 500 and 1500 W, medium plasma power plasma density
8 between 1E9 and 1E11 cm⁻³, a NH₃ flow between 50 and 300 sccm, a
9 H₂ flow between 50 and 300 sccm and a pressure between 80 and
10 800 mTorr. Typical process parameters are power 1000 W and a NH₃
11 flow 100 sccm, H₂ flow about 200 sccm and a pressure 100 mTorr
12 (all values range +/- 5).

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15 **C. 3rd embodiment - NH₃ and N₂**

16 The 3RD embodiment uses NH₃ and N₂ with a power in
17 between 500 and 1500 W, medium plasma power plasma density
18 between 1E9 and 1E11 cm⁻³, a NH₃ flow between 50 and 300 sccm
19 and a N₂ flow between 50 and 300 sccm and a pressure between 80
20 and 800 mTorr. Typical process is power 1000 W and a NH₃ flow 67
21 sccm, N₂ flow about 266 sccm, and a pressure 100 mTorr (all
values range +/- 5).

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23 **D. Optional CO and O₂**

24 All embodiments of the invention's NH₃ containing
25 etch can include additional CO and O₂ flows. The CO and O₂ are
26 thought to remove polymer from the low K layer sidewalls and can
create bowed (non vertical) sidewall profiles.

1 **E. Medium density process and Tool**

2 It is important to realize that the processes (all
3 embodiments) are preferably performed in a medium plasma
4 density between 1E9 and 1E11 cm⁻³. This is contrast with High
5 density plasma between 1.1E11 and 1E12 cm⁻³ . The invention can
6 be performed in a medium density tool, TEL's Rie tools models
7 DRM and SCCM. Thus the process in DRM should also work for SCCM
8 in a similar way.

9 The invention's medium density tools contrast with
10 High density plasma tools (plasma density between 1E11 and 1E12
11 cm⁻³) such as Applied Materials IPS and LAM's TCP 9100.

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II. Invention's hard mask etch step

26 Below are example process for single and dual
27 damascene structure. Any of the hard mask (HM) layers or stop
28 layers (e.g., via and trench liner stop layers) can be etched by
29 the following process.

30 The hard mask (HM) or stop layer etch step
31 preferably comprises: a CF₄ /O₂ /Ar or C₄F₈/O₂ /Ar etch flow with
32 a power between 1000 and 1500 W, a pressure between 40 and 50
33 mTorr and a CF₄ flow between 40 and 80 sccm (C4H8 between 8 and
34 12 sccm), O₂ flow between 5 and 20 sccm and Ar flow between 100
35 and 200 sccm, and medium plasma density between 1E9 and 1E11
36 cm⁻³.

1 **III. Single Damascene structure**

2 FIGS 1 and 2 show an option for a single damascene
3 structure.

4 A semiconductor structure 10 14 is provided.
5 Semiconductor Structure 10 is understood to possibly include a
6 semiconductor wafer 10, active and passive devices formed within
7 the wafer; and insulating and conductive layers (e.g., 14)
8 formed on the wafer surface. For example, layer 14 can be an
9 insulating layer such as an inter metal dielectric (IMD) layer
10 or an etch stop layer.

11 Over the substrate 10 the following layers are
12 preferably formed. A stop liner layer 20 preferably with a
13 thickness of between about 300 and 500 Å. Next, we form a first
14 low k organic inter metal dielectric (IMD) layer 24 preferably
15 with a thickness between 2000 and 4000 Å. Over that, we form a
16 hardmask layer 30 with a thickness between 500 and 2500 Å. The
17 stop liner and hard mask layers can be made of silicon oxide,
18 Silicon oxynitride(SiON), carbide or Silicon nitride (SiN) and
19 are preferably formed of SiN. Next, we form a resist layer 40
20 with a first opening 44.

21 The wafer is placed in an etch tool. The following
22 etch steps are preferably performed insitu.

23 **A. HM open etch step**

24 A hard mask (HM) open etch step is performed to etch
25 thru the HM layer 30. The HM etch step preferably comprises: a
26 CF₄ /O₂ /Ar or C₄F₈/O₂ /Ar etch with a power between 1000 and 1500
27 W, a pressure between 40 and 50 mTorr and a CF₄ flow between 40
28 and 80 sccm (C4H8 between 8 and 12 sccm), O₂ flow between 5 and
29 20 sccm and Ar flow between 100 and 200 sccm.

1 **B. organic Low K dielectric etch step**

2 Next, we etch thru organic Low K dielectric layer 24
3 using one of invention's embodiments for the NH₃ based etch.
4 (See above). During the etch, the photoresist can be removed
5 (e.g., demonstrated NH₃ based resist ashing).

6 **C. Stop liner etch**

7 Next, a stop liner etch step is performed preferably
8 using the following parameters: a CH_xF_y/O₂ /Ar (such as CH₂F₂ /O₂
9 /Ar or CHF₃ /O₂ /Ar flow) with a RF power between 300 and 500 W,
10 pressure between 30 and 40 mtorr, CH₂F₂ flow between 10 and 20
11 sccm (CHF₃ between 10 and 20 sccm), O₂ flow between 5 and 20
12 sccm, and Ar flow between 100 and 200 sccm.

13 FIG 2 shows the structure after the etch steps and
14 opening 50 is formed.

15 **IV. dual Damascene process**

16 FIGS 3, 4 and 5 show a preferred process for a dual
17 damascene process.

18 FIG 3 shows the following structure:

19 Substrate 10 (e.g., SI wafer)
20 dielectric layer 114 (e.g., inter metal dielectric)
21 via stop layer - thickness between 300 and 500 Å
22 first organic IMD layer 128 - thickness between 3000 and
23 5000 Å
24 trench stop layer 134 - (optional) thickness between 0 and
25 500 Å
26 organic IMD trench layer (second IMD layer)- thickness
27 between 3000 and 5000 Å.
28 second hard mask 144 - 500 and 1500 Å
29 first hard mask 148 - 1500 and 2500 Å

1 The hard mask (HM) 144 148 and stop layers 122 134
2 can be formed of silicon oxide, SiON, carbide or SIN and are
3 preferably formed of silicon nitride (SiN).

4 **A. HM1 open for via**

5 As shown in FIG 3, in a first etch step, the HM1 148
6 is etched to form a first HM opening. The hard mask open etch
7 is the same as describe above in the single damascene process.

8 **B. Via etch in trench layer with resist removal**

9 The next etch step is a via etch of the second
10 organic low - k inter metal dielectric layer 138 to form first
11 opening 154 (See FIG 3). During the etch, the photoresist can
12 be removed (e.g., demonstrated NH₃ based resist ashing). .

13 Any of the invention's NH₃ based etch embodiments
14 can be used.

15 **C. Trench stop layer 134 & HM 2 144 etch**

16 As shown in FIG 4, a trench stop layer 134 & HM2 144
17 etch step is performed to form HM opening 155 and to remove the
18 trench stop layer 134 in opening 154. This step can the same
19 etch as the HM open etch steps. See above.

20 **D. Trench and via etch**

21 As shown in FIG 5, the trench opening 164 and via
22 opening 160 are formed by an etch using the HM1 148 and trench
23 stop 134 as etch masks. The etch etches the organic low k layers
24 138 and 128 to form trench opening 164 and via opening 160. The
25 etch uses the invention's NH₃ containing etch.

1 **E. *trench liner 134 and via stop liner 122 etch***

2 Still referring to FIG 5, the trench liner 134 and
3 via stop liner 122 are etched to remove the trench liner 134 and
4 via stop liner 122 in the openings 164 and 160. The trench liner
5 etch is the same as describe above in the single damascene
6 process (E.g., CH₂F₄/O₂ /AR or CHF₄/O₂ /Ar etch).

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8 **F. *Benefits of the invention***

9 The invention's NH₃ containing plasma etch etches
10 organic Low- k materials unexpectedly well and fast. This
11 increases the etch rate without forming polymers and allows for
12 vertical sidewalls of the low- k material.

13 The invention's NH₃ only etch had a 30 to 80% high
14 etch rate than conventional N₂/H₂ etches of low-k materials
15 like Silk TM (e.g., PAE containing dielectric layers).

16 **V. Examples**

17 The inventors performed the following experiments.

18 **Etch rate comparison**

19 Gas flow ratio	Etch rate (K Å/min)
20 100 N ₂ /300 H ₂	1.6
21 200 NH ₃	3
22	
23 50 N ₂ /350 H ₂	1.4
24 100 NH ₃ /200 H ₂	2.4
25	
26 100 NH ₃ /200 H ₂	1.7
27 67NH ₃ /366 H ₂	2.6

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2 With same atomic ratio, the invention's NH₃ based
3 chemistry produced a higher etch rate.

4 Unless explicitly stated otherwise, each numerical
5 value and range should be interpreted as being approximate as if
6 the word about or approximately preceded the value of the
7 value or range.

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10 In the above description numerous specific details
11 are set forth such as flow rates, pressure settings,
12 thicknesses, etc., in order to provide a more thorough
13 understanding of the present invention. It will be obvious,
14 however, to one skilled in the art that the present invention
15 may be practiced without these details. In other instances,
16 well known process have not been described in detail in order to
17 not unnecessarily obscure the present invention. Also, the flow
18 rates in the specification can be scaled up or down keeping the
19 same molar % or ratios to accommodate difference sized reactors
20 as is known to those skilled in the art.

21 Although this invention has been described relative
22 to specific insulating materials, conductive materials and
23 apparatuses for depositing and etching these materials, it is
24 not limited to the specific materials or apparatuses but only to
25 their specific characteristics, such as conformal and non-
26 conformal, and capabilities, such as depositing and etching, and
27 other materials and apparatus can be substituted as is well
28 understood by those skilled in the microelectronics arts after
29 appreciating the present invention

1 Within the present invention, the substrate may be a
2 substrate employed within a microelectronics fabrication
3 selected from the group including but not limited to integrated
4 circuit microelectronics fabrications, solar cell
5 microelectronics fabrications, ceramic substrate
6 microelectronics fabrications and flat panel display
7 microelectronics fabrications. Although not specifically
8 illustrated within the schematic cross-sectional diagram of Fig.
9 1, the substrate 10 may be the substrate itself employed within
10 the microelectronics fabrication, or in the alternative, the
11 substrate may be the substrate employed within tile
12 microelectronics fabrication, where the substrate has formed
13 thereupon or thereover any of several additional
14 microelectronics layers as are conventionally employed within
15 the microelectronics fabrication. Such additional
16 microelectronics layers may include, but are not limited to,
17 microelectronics conductor layers, microelectronics
18 semiconductor layers and microelectronics dielectric layers.

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20 While the invention has been particularly shown and
21 described with reference to the preferred embodiments thereof,
22 it will be understood by those skilled in the art that various
23 changes in form and details may be made without departing from
24 the spirit and scope of the invention. It is intended to cover
25 various modifications and similar arrangements and procedures,
26 and the scope of the appended claims therefore should be
27 accorded the broadest interpretation so as to encompass all such
28 modifications and similar arrangements and procedures.

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2 What is claimed is:

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